

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-158035

(43)Date of publication of application : 31.05.2002

(51)Int.Cl. H01M 10/40

H01M 4/02

H01M 4/58

(21)Application number : 2000-353543

(71)Applicant : MITSUI CHEMICALS INC

(22)Date of filing : 20.11.2000

(72)Inventor : HIBARA AKIO
MATSUOKA OSAMU

(54) NON-AQUEOUS ELECTROLYTE AND SECONDARY BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a non-aqueous electrolyte that suppresses reduction decomposition of electrolyte at storage in high temperature and restrains deterioration of battery property and that gives superior load characteristics and low temperature property to the battery, and a secondary battery containing this non- aqueous electrolyte.

SOLUTION: In an electrochemical cell which uses the basal face of high orientation pyrolytic graphite(HOPG) as a working electrode and metal lithium as a counter electrode for a reference electrode, and a non-aqueous electrolyte as an electrolyte, a non-aqueous electrolyte made of non-aqueous solvent and electrolyte having a strength of 200 $\mu\text{A}/\text{cm}^2$ or less of reduction peak appearing between 0.6 V-0.3 V at the first cycle that sweeps potential of the working electrode at the room temperature at a speed of 10 mV/sec. at 3.0 V-0 V-3.0 V is used and a non-aqueous electrolyte secondary battery using this electrolyte is provided. The desirable manner of the non-aqueous electrolyte is that vinylene carbonate and an additive that suppresses specific reduction decomposition reaction of the electrolyte happening on the negative electrolyte are contained.

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the INPIT, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

Translated: 05:32:39 JST 08/29/2008

Dictionary: Last updated 08/08/2008 / Priority: 1. Chemistry / 2. Mechanical engineering

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] In the Electrochemistry Sub-Division cell which makes an operation pole the Bex Sall side of your kind consideration tropism pyrolytic graphite (HOPG), considers it as a counter electrode by making metal lithium into a reference pole, and uses nonaqueous electrolyte as an electrolyte Nonaqueous electrolyte which becomes the first cycle eye which carries out the electric potential sweep of the electric potential of an operation pole to 3.0V-0V-3.0V at 10mV/second in velocity in a room temperature (25 degrees C) from the nonaqueous solvent with which hardness of the reduction peak which appears between 0.6V-0.3V is characterized by being two or less 200 uA/cm, and an electrolyte.

[Claim 2] this -- the nonaqueous electrolyte according to claim 1 characterized by the hardness of the reduction peak which appears between 0.6V-0.3V being two or less 150 uA/cm.

[Claim 3] this -- the nonaqueous electrolyte according to claim 1 characterized by the hardness of the reduction peak which appears between 0.6V-0.3V being two or less 100 uA/cm.

[Claim 4] Nonaqueous electrolyte according to claim 1 to 3 characterized by said nonaqueous electrolyte containing as an additive at least one sort of compounds chosen from the compound or benzenesulfonic acid derivative which has a norbornene frame.

[Claim 5] Said nonaqueous electrolyte Vinyl ethylene carbonate, divinyl ethylene carbonate, Divinyl sulfone, JIMECHIPIN, norbornene dicarboxylic acid anhydride, Maleic acid anhydride, diethylene glycol acid anhydride, a sulfo benzene carboxylic anhydride, Nonaqueous electrolyte according to claim 1 to 3 characterized by including as an additive sulfo benzene carboxylate, a benzene disulfon acid dilithium salt, and at least one sort of compounds chosen from benzene disulfon acid ester.

[Claim 6] Nonaqueous electrolyte according to claim 1 to 5 characterized by said nonaqueous electrolyte containing vinylene carbonate further.

[Claim 7] Nonaqueous electrolyte according to claim 1 to 6 characterized by said nonaqueous solvent being a nonaqueous solvent containing an ester solvent.

[Claim 8] Nonaqueous electrolyte according to claim 4 to 7 characterized by containing the amount of said additive 0.01 to 2weight % to the whole nonaqueous electrolyte.

[Claim 9] Nonaqueous electrolyte according to claim 6 to 8 characterized by containing the amount of vinylene carbonate 0.05 to 5weight % to the whole nonaqueous electrolyte.

[Claim 10] Nonaqueous electrolyte according to claim 7 to 9 characterized by said ester solvents being cyclic ester and/or chain-like carbonate.

[Claim 11] Nonaqueous electrolyte according to claim 10 characterized by said cyclic ester being either of ethylene carbonate, propylene carbonate, butylene carbonate, gamma butyrolactone, 1, and 4-butane sultone, or its mixture.

[Claim 12] Nonaqueous electrolyte according to claim 10 or 11 characterized by said chain-like carbonate being either dimethyl carbonate, diethyl carbonate or methylethyl carbonate and its mixture.

[Claim 13] Nonaqueous electrolyte according to claim 10 to 12 characterized by the rates of a bulk density in the nonaqueous solvent of said cyclic carbonate and chain-like carbonate being 15:85-55:45.

[Claim 14] Nonaqueous electrolyte according to claim 1 to 13 characterized by said electrolyte being lithium salt.

[Claim 15] Nonaqueous electrolyte according to claim 14 characterized by lithium salt being LiPF₆.

[Claim 16] The cell containing nonaqueous electrolyte according to claim 1 to 15.

[Claim 17] The negative electrode which contains metal lithium, a lithium inclusion alloy, the carbon material in

which dope and dedope of a lithium ion are possible, or the metal oxide in which dope and dedope of a lithium ion are possible as negative electrode active material, The lithium secondary battery characterized by including the positive electrode which contains either a transition metal oxide, transition metal sulfide, the multiple oxide of lithium and a transition metal, a conductive polymer, carbon materials or these mixtures as positive active material, and one of nonaqueous electrolyte according to claim 1 to 16.

[Claim 18] The lithium secondary battery according to claim 17 characterized by for negative electrode active material being the carbon material in which dope and dedope of a lithium ion are possible, and the spacing distance (d002) in the field (002) measured with the X-ray analysis in this carbon material being 0.340nm or less.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to nonaqueous electrolyte excellent in charge-and-discharge characteristics, and the secondary battery using it. It is related with the nonaqueous electrolyte containing the additive which inhibits the specific reductive cleavage of the electrolyte which starts a detail on vinylene carbonate and a negative electrode more, and the secondary battery using it.

[0002]

[Background of the Invention] The cell using nonaqueous electrolyte is high tension, and has a high energy density, and since reliability, such as keeping, is high, it is widely used as a power source of household electronic appliances.

[0003] There is a nonaqueous electrolyte secondary battery as such a cell, and the representation is a rechargeable lithium-ion battery. The carbonate compound with high permittivity is known as a nonaqueous solvent used for it, and the activity of various carbonate compounds is proposed. As an electrolyte, moreover, said high permittivity carbonate compound solvents, such as propylene carbonate and ethylene carbonate, The solution which mixed electrolytes, such as LiBF₄, LiPF₆, LiClO₄, LiAsF₆, LiCF₃SO₃, and Li₂SiF₆, is used for the mixed solvent with hypoviscosity solvents, such as diethyl carbonate.

[0004] On the other hand, investigation of the electrode is also advanced aiming at high-capacity-izing of a cell, and the occlusion of lithium and the carbon material which can be emitted are used as a negative electrode of a rechargeable lithium-ion battery. Since it has the features, like discharge potential is flat and there is, especially high crystallinity carbon, such as graphite, is adopted as a negative electrode of most rechargeable lithium-ion batteries marketed now.

[0005] When using high crystallinity carbon, such as graphite, for a negative electrode, as a high permittivity nonaqueous solvent for electrolytes If propylene carbonate and 1 and 2-butylene carbonate are used, in the edge face of graphite, the reductive cleavage of a solvent will occur at the time of first time charge, and the insertion reaction to graphite of the lithium ion which is an active material will become difficult to advance. As a result, it is known that decline in first-time charge-and-discharge efficiency will take place. (Electrochem.Soc., 146(5)1664-1671 (1999), etc.)

[0006] For this reason, as a nonaqueous solvent of the high permittivity used for an electrolyte although it is a solid in ordinary temperature By reductive cleavage's mixing the ethylene carbonate which does not happen easily continuously to propylene carbonate, and restricting the content of the propylene carbonate in an electrolyte, the attempt which suppresses the reductive cleavage of a nonaqueous solvent is made. Making an electrolyte contain vinylene carbonate as an additive which inhibits the reductive cleavage of the solvent on a negative electrode is proposed. It is shown by by making vinylene carbonate contain that the storage characteristics of a cell are improved (JP,7-192756,A). The cycle life of a cell improves by adding vinylene carbonate (JP,7-192760,A). Moreover, it is reported that the propylene carbonate which receives reduction decomposition in the edge face of a graphite negative electrode can be used (the international conference on a ten younger brother lithium battery, abstract No.286). Since vinylene carbonate makes propylene carbonate usable, acting on the edge face of a graphite negative electrode is suggested.

[0007] Although improvement in the charge-and-discharge characteristics of a cell has been achieved by these cures, the electrolyte which improves further lowering of the load characteristic of a cell at the time of repeating elevated-temperature preservation and a charge-and-discharge cycle and lowering of cell capacity is called for.

[0008] By the way, the graphite material has taken the configuration in which the highly-developed carbon

condensed-ring flat surface was piled up, and calls the field where the edge face and the carbon condensed-ring flat surface carried out the orientation of the field in which the end face of this carbon condensed ring carried out the orientation the Bex Sall side. This edge face and the Bex Sall side have electronic conductivity, and both sides can carry out reduction decomposition of the electrolyte electrochemically. Although some reports should be beginning to do about reduction disassembly of the electrolyte in the Bex Sall side (the collection of -440 or Electrochemistry Communicationm2 (2000) 436 2000 Electrochemical Society of Japan autumn convention summaries, two A17, 21 pages) The additive for electrolytes which controls the reduction decomposition in respect of Bex Sall is not reported until now, either. [0009]

[Problem to be solved by the invention] In order that this invention may respond to the aforementioned request, it aims at offering the electrolyte which controls reduction disassembly of an electrolyte at the time of elevated-temperature preservation, and controls deterioration of a battery characteristic. Moreover, it aims at offering the nonaqueous electrolyte which gives a load characteristic and low-temperature characteristics excellent in the cell. Furthermore, it aims at offer of the secondary battery containing this nonaqueous electrolyte. [0010]

[Means for solving problem] In order for this invention person to solve the above-mentioned technical problem, when it inquired wholeheartedly, he found out further that life characteristics, such as an elevated-temperature retention test of a cell and a cycle check, could be improved by controlling reduction disassembly of the electrolyte in the edge face on a graphite negative electrode, and both sides of the Bex Sall side. [0011] Namely, this invention is set in the Electrochemistry Sub-Division cell which makes an operation pole the Bex Sall side of your ** kind consideration tropism pyrolytic graphite (HOPG), considers it as a counter electrode by making metal lithium into a reference pole, and uses nonaqueous electrolyte as an electrolyte. The hardness of the reduction peak which appears between 0.6V-0.3V in the first cycle eye which carries out the electric potential sweep of the electric potential of an operation pole to 3.0V-0V-3.0V at 10mV/second in velocity in a room temperature (25 degrees C) offers the nonaqueous electrolyte which consists of a nonaqueous solvent which is two or less 200 uA/cm, and an electrolyte.

[0012] ** Nonaqueous electrolyte given in ** characterized by the hardness of the reduction peak which appears between said 0.6V-0.3V being two or less 150 uA/cm is the desirable mode of this invention. [0013] ** said -- this -- nonaqueous electrolyte given in ** characterized by the hardness of the reduction peak which appears between 0.6V-0.3V being two or less 100 uA/cm is the desirable mode of this invention. [0014] ** Nonaqueous electrolyte given in either ** in which said nonaqueous electrolyte contains as an additive at least one sort of compounds chosen from the compound or benzenesulfonic acid derivative which has a norbornene frame - ** is the desirable mode of this invention. .

[0015] Said nonaqueous electrolyte ** Vinyl ethylene carbonate, divinyl ethylene carbonate, Divinyl sulfone, JIMECHIPIN, norbornene dicarboxylic acid anhydride, Maleic acid anhydride, diethylene glycol acid anhydride, a sulfo benzene carboxylic anhydride, Nonaqueous electrolyte given in either ** which contains as an additive sulfo benzene carboxylate, a benzene disulfon acid dilithium salt, and at least one sort of compounds chosen from benzene disulfon acid ester - ** is the desirable mode of this invention. [0016] ** Said nonaqueous electrolyte is the mode of this invention also with desirable nonaqueous electrolyte given in either ** which contains vinylene carbonate further - **. [0017] ** Nonaqueous electrolyte given in either ** which is the nonaqueous solvent with which said nonaqueous solvent contains an ester solvent - ** is also the desirable mode of this invention. [0018] ** Also in nonaqueous electrolyte given in ** which are cyclic ester and/or chain-like carbonate, said ester solvent is the desirable mode of this invention.

[0019] ** [0020] which is the desirable mode of this invention also at nonaqueous electrolyte given in either ** said whose electrolyte is lithium salt - ** Moreover, this invention offers the cell containing the above mentioned nonaqueous electrolyte. [0021] The negative electrode in which this invention furthermore contains metal lithium, a lithium inclusion alloy, the carbon material in which dope and dedope of a lithium ion are possible, or the metal oxide in which dope and dedope of a lithium ion are possible as negative electrode active material, The lithium secondary battery containing the positive electrode which contains either a transition metal oxide, transition metal sulfide, the multiple oxide of lithium and a transition metal, a conductive polymer, carbon materials or these mixtures as positive active material, and the above mentioned nonaqueous electrolyte is offered.

[0022] The lithium secondary battery said whose negative electrode active material is the carbon material in which dope and dedope of a lithium ion are possible and whose spacing distance (d002) in the field (002)

measured with the X-ray analysis in this carbon material is 0.340nm or less is the desirable mode of this invention.

[0023]

[The concrete form of invention implementation] Next, the nonaqueous electrolyte concerning this invention and the nonaqueous electrolyte secondary battery using this nonaqueous electrolyte are explained concretely.

[0024] In the Electrochemistry Sub-Division cell which the electrolyte of this invention makes an operation pole the Bex Sall side of your kind consideration tropism pyrolytic graphite (HOPG), makes metal lithium a reference pole and a counter electrode, and uses nonaqueous electrolyte as an electrolyte In a room temperature (25 degrees C), the electric potential of an operation pole [3.0V-0V-3.0V] The reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on a HOPG electrode in the first cycle eye which carries out an electric potential sweep at the rate of 10 mV/se is nonaqueous electrolyte which consists of a nonaqueous solvent which is two or less 200 uA/cm, and an electrolyte. moreover, the cell by which this invention contains this nonaqueous electrolyte -- a lithium secondary battery is offered preferably.

[0025] In order to evaluate the reduction decomposition characteristics of the electrolyte of the edge face on a negative electrode, and the Bex Sall side, electric current electric potential (CV) measurement which made the operation pole your kind consideration tropism pyrolytic graphite (code HOPG) electrode is performed. In this invention, the cell which was further excellent in the life characteristic can be obtained in CV measurement in a HOPG electrode by using the electrolyte which controls both the reduction peak resulting from an edge face, and the reduction peak resulting from the Bex Sall side. If reduction decomposition takes place to the electrolyte of the edge face on a negative electrode, and the Bex Sall side, the energy of a cell falls, and a decomposition product will accumulate on an electrode surface and the load characteristic of a cell and low-temperature characteristics will fall.

[0026] Although it is desirable that it is two or less 200 uA/cm as for the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on the HOPG electrode which the electrolyte of this invention described above, it is two or less 150 uA/cm more preferably, and is two or less 100 uA/cm still more preferably.

[0027] The nonaqueous electrolyte of this invention is nonaqueous electrolyte which consists of a nonaqueous solvent and an electrolyte. Although it can be used choosing from the well-known nonaqueous solvent used for cells suitably as a nonaqueous solvent In order to satisfy the requirements for the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on the above-mentioned above mentioned HOPG electrode, the choice of a suitable nonaqueous solvent, an electrolyte, and an additive is called for.

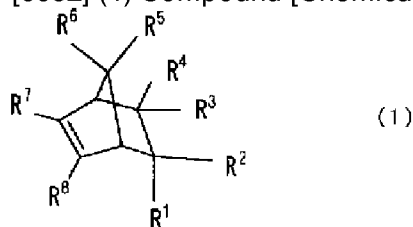
[0028] In this invention, in order to satisfy the requirements for the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on the above-mentioned above mentioned HOPG electrode, it is desirable to use the selected additive.

[0029] As an example of the cyclic carbonate and chain-like carbonate which are later mentioned as a suitable example of a nonaqueous solvent When the electrolyte which carried out 1 mol/l dissolution of LiPF₆ as an electrolytic example further is explained using the mixture of the rate of 4:6 bulk densities of ethylene carbonate and methylethyl carbonate, on condition of a **** The hardness of the reduction peak which appears between 0.6V-0.3V is about 250uA/cm² for a peak top.

[0030] Therefore, it is desirable to add the additive which controls reduction Py who appears between 0.6V-0.3V resulting from the Bex Sall side on a HOPG electrode to this electrolyte.

[0031] The following compounds can be illustrated as an additive which can control the reduction peak which appears in additive this invention between 0.6V-0.3V resulting from the Bex Sall side on a HOPG electrode.

[0032] (1) Compound [Chemical formula 1] which has a norbornene frame

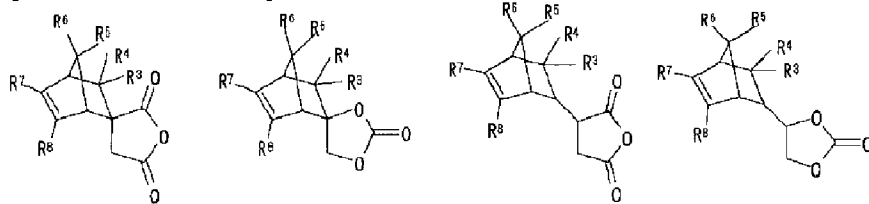


([at least one of / R1 or R2 / a formula is the substituent containing annular carbonate or annular anhydrous carboxylic acid, and / R3-R8]) It may be mutually the same, or you may differ, and it is chosen out of the organic group of hydrogen, halogen, and carbon numbers 1-10. As an example of a compound expressed with a

general formula (1), the thing of the following configurations is illustrated more by the detail.

[0033]

[Chemical formula 2]



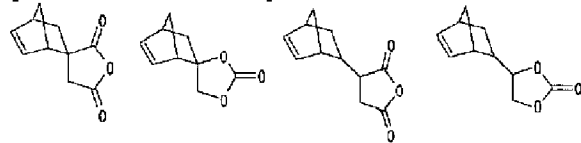
[0034] As an organic group of carbon numbers 1-10, a hydrocarbon group, a halogenated hydrocarbon machine, the hydrocarbon group containing a hetero atom, the halogenated hydrocarbon machine containing a hetero atom, etc. are mentioned. Oxygen, nitrogen, sulfur, a phosphorus, boron, etc. are mentioned as a hetero atom. Fluorine and chlorine are mentioned as halogen.

[0035] As an organic group of carbon numbers 1-10, specifically A trifluoromethyl machine, A trifluoro methoxy group, a trifluoroethyl machine, a trifluoroethoxy machine, A pentafluoroethyl machine, a pentafluoro ethoxy group, a methyl group, a methoxy group, An ethyl group, an ethoxy group, a vinyl group, a BINIROKISHI machine, an ethynyl group, a propyl group, Pro PIROKISHI mind, an isopropyl group, 1-propenyl machine, 2-propenyl machine, 1-propynyl machine, 2-propynyl group, an allyloxy machine, a pro PAL GIROKISHI machine, Butyl, a butoxy machine, sec-butyl, t-butyl, 1-butenyl group, 2-butenyl group, 3-butenyl group, a 2-methyl 2-propenyl machine, 1-methylene propyl group, a 1-methyl 2-propenyl machine, 1, 2-dimethyl vinyl group, 1-butylnyl machine, 2-butylnyl machine, 3-butylnyl machine, a BUTENIROKISHI machine, A BUCHINIROKISHI machine, a pentyl group, 1-methylbutyl machine, 2-methylbutyl machine, 3-methylbutyl machine, 1-methyl 2-methylpropyl machine, 2, and 2-dimethyl propyl group, a phenyl group, a phenoxy group, a methylphenyl machine, an ethyl phenyl group, a vinyl phenyl group, an ethynyl phenyl group, a fluoro vinyl phenyl group, a fluoro ethynyl phenyl group, A fluoro phenyl group, a difluoro phenyl group, a trifluoro methylphenyl machine, A chlorophenyl machine, a fluoro methoxypheny machine, a difluoro methoxypheny machine, a methoxycarbonyl group, an ethoxycarbonyl machine, a trifluoro ethoxycarbonyl machine, a trifluoromethyl carbonyl group, etc. are illustrated.

[0036] As for the carbon number of the soluble point to the electrolyte of a norbornene derivative with annular carbonate or annular anhydrous dicarboxylic acid to a substituent to a substituent, it is desirable that it is three or less among the substituents illustrated above.

[0037] Specifically as a norbornene derivative with above mentioned annular carbonate or annular anhydrous dicarboxylic acid to a substituent, the compound shown below can be mentioned.

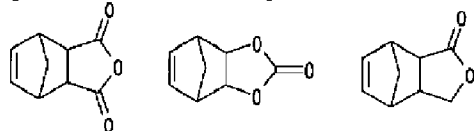
[Chemical formula 3]



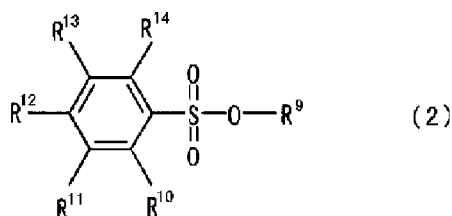
[0038] What is shown below is illustrated as a compound which has norbornene frames other than said general formula (1).

[0039]

[Chemical formula 4]



[0040] (2) Benzenesulfonic acid derivative [Chemical formula 5]



(R9 is an alkyl group or a metal.) It may be mutually the same, or you may differ, and may combine with each other, and R10-R14 are chosen from hydrogen, halogen, a sulfonate machine, a sulfonic acid metal machine, a carboxylate machine, a carboxylic acid metal machine, and the organic group of carbon numbers 1-10.

[0041] In a formula (2), as a metal, an alkali metal, an alkaline earth metal, etc. are mentioned and especially an alkali metal is desirable. As an alkali metal, lithium, sodium, and potassium are illustrated and, specifically, lithium is the most desirable.

[0042] As an organic group of carbon numbers 1-10, a hydrocarbon group, a halogenated hydrocarbon machine, the hydrocarbon group containing a hetero atom, the halogenated hydrocarbon machine containing a hetero atom, etc. are mentioned. Oxygen, nitrogen, sulfur, a phosphorus, boron, etc. are mentioned as a hetero atom. Fluorine and chlorine are mentioned as halogen.

[0043] As an organic group of carbon numbers 1-10, specifically A trifluoromethyl machine, A trifluoro methoxy group, a trifluoroethyl machine, a trifluoroethoxy machine, A pentafluoroethyl machine, a pentafluoro ethoxy group, a methyl group, a methoxy group, An ethyl group, an ethoxy group, a vinyl group, a BINIROKISHI machine, an ethynyl group, a propyl group, Pro PIROKISHI mind, an isopropyl group, 1-propenyl machine, 2-propenyl machine, 1-propynyl machine, 2-propynyl group, an allyloxy machine, a pro PAL GIROKISHI machine, Butyl, a butoxy machine, sec-butyl, t-butyl, 1-butenyl group, 2-butenyl group, 3-butenyl group, a 2-methyl 2-propenyl machine, 1-methylene propyl group, a 1-methyl 2-propenyl machine, 1, 2-dimethyl vinyl group, 1-butyryl machine, 2-butyryl machine, 3-butyryl machine, a BUTENIROKISHI machine, A BUCHINIROKISHI machine, a pentyl group, 1-methylbutyl machine, 2-methylbutyl machine, 3-methylbutyl machine, 1-methyl 2-methylpropyl machine, 2, and 2-dimethyl propyl group, a phenyl group, a phenoxy group, a methylphenyl machine, an ethyl phenyl group, a vinyl phenyl group, an ethynyl phenyl group, a fluoro vinyl phenyl group, a fluoro ethynyl phenyl group, A fluoro phenyl group, a difluoro phenyl group, a trifluoro methylphenyl machine, A chlorophenyl machine, a fluoro methoxypheny machine, a difluoro methoxypheny machine, a methoxycarbonyl group, an ethoxycarbonyl machine, a trifluoro ethoxycarbonyl machine, a trifluoromethyl carbonyl group, etc. are illustrated.

[0044] As for the carbon number of the soluble point to the electrolyte of phenyl sulfonic acid or a phenyl sulfonic acid metal to a substituent, it is desirable that it is three or less among the substituents of R10-R14 which were illustrated above.

[0045] It is desirable for at least one of R10-R14 to be a sulfonate machine or a sulfonic acid metal machine especially in this invention.

[0046] Specifically, the compound shown below can be mentioned as the above mentioned phenyl sulfonic acid. Indicating methyl ester, ethyl ester, propyl ester, butylester, phenyl ester, trifluoro methyl ester, or pentafluoro propyl ester to be ester below is shown.

[0047] Sulfobenzonic acid anhydride, naphthalene sulfonate, benzenesulfonic acid ester, BENZENJI (sulfonate), a benzene bird (sulfonate), Sulfobenzonic acid diester, toluenesulfonic acid ester, TORUENJI (sulfonate), A toluene bird (sulfonate), benzoic acid (sulfo (methyl)) diester, Trifluoromethyl benzene (sulfonate), trifluoromethyl BENZENJI (sulfonate), A trifluoromethyl benzene bird (sulfonate), benzoic acid (trifluoromethyl (sulfo)) diester, Naphthalene sulfonic acid lithium salt, benzenesulfonic acid lithium salt, Trifluoromethyl benzenesulfonic acid lithium salt, a benzene disulfon acid dilithium salt, A trifluoromethyl benzene disulfon acid dilithium salt, benzene Trisul Hong acid bird lithium salt, A sulfobenzonic acid dilithium salt, methoxycarbonyl benzenesulfonic acid lithium salt, ethoxycarbonyl sulfonic acid lithium salt, vinyloxycarbonyl sulfonic acid lithium salt, allyloxy carbonyl sulfonic acid lithium salt, Ethynyl oxycarbonyl sulfonic acid lithium salt, propargyl oxycarbonyl benzenesulfonic acid lithium salt, Benzene disulfon acids and sulfobenzonic acid are desirable especially in trifluoroethyl oxycarbonyl benzenesulfonic acid lithium salt, toluenesulfonic acid lithium salt, a toluene disulfon acid dilithium salt, and the phenyl sulfonic acid derivative illustrated above.

[0048] In addition to the compound illustrated by the above (1) and (2), (3) In addition, vinyl ethylene carbonate, Divinyl ethylene carbonate, propenyl ethylene carbonate, butenyl ethylene carbonate, methylvinyl ethylene

carbonate, dipropenyl ethylene carbonate, divinyl sulfone, JIMECHIPIN, maleic acid anhydride, diethylene glycol acid anhydride, etc. are illustrated.

[0049] Among the additives which can control the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on the HOPG electrode illustrated above, especially Vinyl ethylene carbonate, divinyl ethylene carbonate, divinyl sulfone, JIMECHIPIN, norbornene dicarboxylic acid anhydride, a sulfo benzene carboxylic anhydride, sulfo benzene carboxylic acid diester, a benzene disulfon acid dilithium salt, and benzene disulfon acid diester are desirable.

[0050] As for the addition of the additive which controls the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on a HOPG electrode, it is desirable that it is 0.05 to 1 weight % still more preferably 0.01 to 2weight % preferably 0.001 to 5weight % to the whole electrolyte.

[0051] In addition to the additive which controls the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on an above-mentioned HOPG electrode, vinylene carbonate can be added in this invention. There is an effect which controls the reduction peak which appears in the first measurement cycle on these conditions between 0.9V-0.6V resulting from the edge face on a HOPG electrode in vinylene carbonate. When only vinylene carbonate is added without using an above-mentioned additive Since it is difficult to control the reduction peak resulting from the Bex Sall side which appears between 0.6V-0.3V In order to control the reduction peak which appears between 0.9V-0.6V resulting from the Bex Sall side and edge face on a HOPG electrode, it is more effective to use both vinylene carbonate and an above-mentioned additive in this invention, and it is desirable.

[0052] As for the addition of the vinylene carbonate which is the above mentioned additive and which can be set, it is desirable that it is 0.1 to 2 weight % still more preferably 0.05 to 5weight % preferably 0.01 to 10weight % to the whole electrolyte.

[0053] As a desirable nonaqueous solvent, cyclic carbonate and/or chain-like carbonate can be mentioned by nonaqueous solvent this invention. As an example of cyclic carbonate, specifically Ethylene carbonate, propylene carbonate, 1, 2-butylene carbonate, 2, 3-butylene carbonate, 1, 2-pentylene carbonate, 2, 3-pentylene carbonate, gamma-butyrolactone, 3-methyl gamma-butyrolactone, 2-methyl gamma-butyrolactone, 1, and 4-butane sultone etc. is mentioned. Ethylene carbonate and propylene carbonate with high permittivity are used in particular suitably. Ethylene carbonate is desirable especially when especially the improvement in a battery life is meant.

[0054] Moreover, two or more sorts may use these cyclic ester, mixing. As a concrete combination, ethylene carbonate and propylene carbonate, Ethylene carbonate, butylene carbonate and ethylene carbonate, and gamma butyrolactone, Ethylene carbonate, propylene carbonate, gamma butyrolactone and ethylene carbonate, 1, 4-butane sultone and ethylene carbonate, propylene carbonate, 1, 4-butane sultone and ethylene carbonate, gamma butyrolactone, 1, 4-butane sultone, etc.

[0055] In the electrolyte of this invention, when also making improvement in low-temperature characteristics give, it is desirable to contain chain-like carbonate in a nonaqueous solvent. As chain-like carbonate, specifically Dimethyl carbonate, methylethyl carbonate, Diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, dipropyl carbonate, methylbutyl carbonate, dibutyl carbonate, ethyl propyl carbonate, methyl trifluoroethyl carbonate, etc. are mentioned. Dimethyl carbonate and methylethyl carbonate with low viscosity, and diethyl carbonate are used in particular suitably. Two or more sorts may use these chains-like carbonate, mixing.

[0056] As combination of the cyclic carbonate of a nonaqueous solvent, and chain-like carbonate, specifically Ethylene carbonate, dimethyl carbonate and ethylene carbonate, and methylethyl carbonate, Ethylene carbonate, diethyl carbonate and ethylene carbonate, propylene carbonate, and dimethyl carbonate, Ethylene carbonate, propylene carbonate, and methylethyl carbonate, Ethylene carbonate, propylene carbonate, and diethyl carbonate, Ethylene carbonate, dimethyl carbonate, and methylethyl carbonate, Ethylene carbonate, dimethyl carbonate, and diethyl carbonate, Ethylene carbonate, propylene carbonate, dimethyl carbonate, and methylethyl carbonate, Ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate and ethylene carbonate, propylene carbonate, methylethyl carbonate, diethyl carbonate, etc. are mentioned.

[0057] expressing the ratio with a bulk density, when mixing cyclic ester and chain-like carbonate -- said cyclic ester:chain-like ester -- 5:95-80:20 -- desirable -- 10:90-70:30 -- it is 15:85-55:45 still more preferably. Since viscosity lifting of an electrolyte is controlled and an electrolytic degree of dissociation is not reduced by making it such a ratio, the conductivity of the electrolyte in connection with the charge-and-discharge characteristics of a cell can be raised. For this reason, the load characteristic in the high load in the ordinary temperature of a cell and the load characteristic in the low temperature of a cell are improvable.

[0058] The desirable nonaqueous solvent concerning this invention contains cyclic ester and/or chain-like ester. Moreover, it is also possible to use the solvent usually widely used as a nonaqueous solvent for cells in addition to them, mixing further.

[0059] In the nonaqueous electrolyte concerning this invention, other solvents other than the above may be included as a nonaqueous solvent, and as other solvents Specifically Methyl formate, ethyl formate, propyl formate, methyl acetate, Ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, Methyl butyrate, valeric acid methyl, trifluoro ethyl acetate, pentafluoro methyl acetate, Chain-like ester, such as trifluoro ethyl acetate and propionic acid trifluoroethyl; Trimethyl phosphate, Phosphoric ester; 1, such as phosphoric acid triethyl, 2-dimethoxyethane, 1, 2-diethoxy ethane, diethylether, wood ether, Chain-like ether; 1, such as methylethyl ether and dipropyl ether, 4-dioxane, 1, 3-dioxolane, tetrahydrofuran, 2-methyl tetrahydrofuran, Amide, such as cyclic ether; dimethylformamides, such as the 3-methyl 1, 3-dioxolane, the 2-methyl 1, and 3-dioxolane, and diethyl formamide; Methyl N, N-dimethyl KABA mate, Chain-like Cava mates, such as Trifluoroethyl N and N-diethyl KABA mate; Annular urea, such as cyclic amide; N, such as annular Cava mate; N-methyl pyrrolidone, such as annular sulfone; N-methyl oxazolidinone, such as a sulfolane, and N-dimethyl imidazolidinone, Sulfur containing compounds, such as divinyl sulfone, a sulfolane, and dimethyl sulfate; ** boron compounds [0060], such as way acid bird methyl, way acid triethyl, way acid tributyl, way acid trioctyl, and way acid bird trimethylsilyl Although what contains at least one sort and said chain-like carbonate among said cyclic ester is proposed in this invention as a desirable combination of the nonaqueous solvent in the case of aiming at improvement in the low-temperature characteristics of a cell It is better to reduce the content of chain-like ester, when aiming at improvement in the flash point of a solvent rather than improvement in low-temperature characteristics. As a combination of a concrete solvent, ethylene carbonate and propylene carbonate, Ethylene carbonate, butylene carbonate and ethylene carbonate, and gamma butyrolactone, Ethylene carbonate, propylene carbonate, and gamma butyrolactone, Ethylene carbonate, 1, 4-butane sultone and ethylene carbonate, propylene carbonate, and 1, 4-butane sultone, Ethylene carbonate, gamma butyrolactone, and 1, 4-butane sultone, Ethylene carbonate, a sulfolane and ethylene carbonate, and trimethyl phosphate, Ethylene carbonate, gamma butyrolactone, trialkyl phosphate and ethylene carbonate, gamma butyrolactone, a sulfolane and ethylene carbonate, gamma butyrolactone, a sulfolane, trialkyl phosphate, etc. are illustrated. In this case, as for addition of chain-like carbonate, it is desirable to restrict to 20% or less by a bulk density.

[0061] The nonaqueous electrolyte of nonaqueous electrolyte this invention consists of an additive which controls the reduction peak which appears between 0.6V-0.3V resulting from the Bex Sall side on a nonaqueous solvent, vinylene carbonate, and a HOPG electrode.

[0062] As an electrolytic example, lithium salt, such as LiPF_6 , $\text{LiPF}_3(\text{CnF}_{2n+1})_3$, LiBF_4 , LiClO_4 , LiAsF_6 , Li_2SiF_6 , $\text{LiC}_4\text{F}_9\text{SO}_3$, and $\text{LiC}_8\text{F}_{17}\text{SO}_3$, is mentioned. Moreover, the lithium salt shown by the following general formula can also be used. LiOSO_2R_8 , $\text{LiN}(\text{SO}_2\text{R}_9)(\text{SO}_2\text{R}_{10})$, $\text{LiC}(\text{SO}_2\text{R}_{11})(\text{SO}_2\text{R}_{12})(\text{SO}_2\text{R}_{13})$, $\text{LiN}(\text{here})(\text{SO}_2\text{OR}_{14})(\text{SO}_2\text{OR}_{15})$ Even if R_8 - R_{15} are mutually the same, they may differ from each other, and they are the perfluoroalkyl machine of carbon numbers 1-6. These lithium salt may be used independently, and may mix and use two or more sorts.

[0063] LiPF_6 , $\text{LiPF}_3(\text{CnF}_{2n+1})_3$, LiBF_4 , LiOSO_2R_8 , $\text{LiN}(\text{SO}_2\text{R}_9)(\text{SO}_2\text{R}_{10})$, $\text{LiC}(\text{SO}_2\text{R}_{11})(\text{SO}_2\text{R}_{12})(\text{SO}_2\text{R}_{13})$, and $\text{LiN}(\text{SO}_2\text{OR}_{14})(\text{SO}_2\text{OR}_{15})$ are [among these] desirable especially. Furthermore, LiPF_6 and LiBF_4 are desirable.

[0064] As for such an electrolyte, it is desirable to contain 0.1-3mol/l. in nonaqueous electrolyte by the concentration of 0.5-2mol/l. preferably.

[0065] It is not only suitable as nonaqueous electrolyte for rechargeable lithium-ion batteries, but it can use the nonaqueous electrolyte concerning above this inventions as nonaqueous electrolyte for primary batteries.

[0066] It is constituted including fundamentally a negative electrode, a positive electrode, and the aforementioned nonaqueous electrolyte, and, as for the nonaqueous electrolyte secondary battery concerning secondary battery this invention, the separator is usually formed between the negative electrode and the positive electrode.

[0067] As negative electrode active material which constitutes a negative electrode, doping and the carbon material which can be dedoped are mentioned in metal lithium, a lithium alloy, and a lithium ion, and dope, the metal oxide which can be dedoped, etc. are mentioned in a lithium ion. Doping and the carbon material which can be dedoped are desirable in a lithium ion also in these. Such a carbon material may be graphite, or may be amorphous carbon, and activated carbon, carbon fiber, carbon black, meso carbon micro beads, natural graphite, etc. are used.

[0068] As negative electrode active material, a carbon material of 0.340nm or less has desirable spacing (d002) of the field (002) measured especially with the X-ray analysis, and the high crystallinity carbon material which has a characteristic with the density near graphite or it which is 1.70g/cm³ or more is desirable. If such a carbon material is used, the energy density of a cell can be made high.

[0069] As positive active material which constitutes a positive electrode, a transition metal oxide or transition metal sulfide, such as MoS₂, TiS₂, MnO₂, and V₂O₅, The multiple oxide which consists of lithium and transition metals, such as LiCoO₂, LiMnO₂, LiMnO₄, LiNiO₂, and LiNi_xCo(1-x) O₂, Conductive polymers, such as poly aniline, poly thiophene, polypyrrole, polyacetylene, the poly acene, and dimercapto thiadiazole / poly aniline complex, etc. are mentioned. Also in these, the multiple oxide which especially consists of lithium and a transition metal is desirable. When a negative electrode is a lithium metal or a lithium alloy, a carbon material can also be used as a positive electrode. Moreover, the mixture of lithium, the multiple oxide of a transition metal, and a carbon material can also be used as a positive electrode.

[0070] A separator is a film which insulates a positive electrode and a negative electrode electrically, and penetrates a lithium ion, and a porous film and polyelectrolyte are illustrated. As a porous film, a fine porosity polymer film is used suitably, and polyolefine, polyimide, and polyvinylidene fluoride are illustrated as construction material. In particular, a porous polyolefin film is desirable and the integral multi-pack film of a porous polyethylene film, a porous polypropylene film or a porous polyethylene film, and polypropylene can specifically be illustrated. As polyelectrolyte, the polymer which dissolved lithium salt, the polymer swollen with the electrolyte, etc. are mentioned. You may use the electrolyte of this invention in order to swell a polymer and to obtain polyelectrolyte.

[0071] Such a nonaqueous electrolyte secondary battery can be formed in configurations cylindrical, a coin type, a square shape, a film type, in addition arbitrary. However, the basic structure of a cell depends and is the same as a configuration, and a design change can be performed according to the object. Next, although the configuration of cylindrical and a coin type cell is explained, what described above the negative electrode active material, the positive active material, and the separator which constitute each cell is used in common.

[0072] For example, in the case of the cylindrical nonaqueous electrolyte secondary battery, through the separator which poured in nonaqueous electrolyte, the negative electrode which applies negative electrode active material to a negative electrode current collection object, and the positive electrode which applies positive active material at a positive electrode current collector are stored at the battery can, where [of winding and a winding body] an electric insulating plate is laid up and down.

[0073] Moreover, the nonaqueous electrolyte secondary battery concerning this invention is applicable also to a coin type nonaqueous electrolyte secondary battery. In the coin type cell, the plate of a disc-like negative electrode, a separator, a disc-like positive electrode and stainless steel, or an aluminium is stored by the coin type cell can, after this order has laminated.

[0074]

[Working example] Although a work example and a comparative example explain this invention more below at a detail, this invention is not restricted at all by these work examples.

[0075] In this invention, CV measurement which made the operation pole your kind consideration tropism pyrolytic graphite (code HOPG) electrode was performed by the following method.

The CV measurement CV measurement which uses a HOPG electrode used metal lithium for the reference pole which is a counter electrode about the cleavage plane (phi5mm) of HOPG (ADOBANZUDO ceramic corporation company make STM-1 grade is used) on the operation pole, and 1.5ml of electrolytes were used. This cell was connected with CV measuring instrument (solartoron1286 electrochemical interface), and electric current electric potential measurement was performed under the conditions of a room temperature (25 degrees C). The measurement voltage range is Li/Li⁺. It was considered as the electric potential sweep cycle turned up to 3.0V-0.0V-3.0V on the basis of electric potential. This electric potential sweep cycle was performed at 10mV/sec in velocity, and the flowing reduction current was measured.

[0076] (Comparative example 1) CV measurement of the first cycle eye of the electrolyte (it is henceforth called a blank electrolyte) which dissolved LiPF₆ of 1 mol/l in the mixed solvent of the bulk density (4:6) of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) was performed. Drawing 1 is drawing having shown the result. In this CV measurement figure, the reduction peak which appears in 0.9-0.6V is a peak resulting from the edge of HOPG, and the reduction peak which appears in 0.6-0.3V is a peak resulting from Bex Sall of HOPG.

[0077] (Comparative example 2) CV measurement of the first cycle eye of the electrolyte which added vinylene carbonate (VC) 2weight % to the blank electrolyte was performed. Drawing 2 is drawing having shown the result. In this CV measurement figure, although it turns out that the reduction peak which appears in 0.9-0.6V

becomes small, and is controlled, the reduction peak which appears in 0.6-0.3V is not controlled at all.

[0078] (Work example 1) CV measurement of the first cycle eye of the electrolyte which added sulfo benzoic acid anhydride 0.5weight % to the blank electrolyte was performed. Drawing 3 is drawing having shown the result.

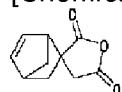
[0079] (Work example 2) CV measurement of the first cycle eye of the electrolyte which added m-benzene disulfon acid dimethyl ester 0.5weight % to the blank electrolyte was performed. Drawing 4 is drawing having shown the result.

[0080] (Work example 3) CV measurement of the first cycle eye of the electrolyte which added benzenesulfonic acid dipotassium salt 0.5weight % to the blank electrolyte was performed. Drawing 5 is drawing having shown the result.

(Work example 4) CV measurement of the first cycle eye of the electrolyte which added norbornene 5 and 6-dicarboxylic acid anhydride 1weight % to the blank electrolyte was performed. Drawing 6 It is drawing having shown the *****.

(Work example 5) CV measurement of the first cycle eye of the electrolyte which added the spiro type norbornyl ***** acid anhydride expressed with the following type by the blank electrolyte 1weight % was performed. Drawing 7 is drawing having shown the result.

[Chemical formula 6]



(Work example 6) CV measurement of the first cycle eye of the electrolyte which added vinyl ethylene carbonate 1weight % to the blank electrolyte was performed. Drawing 8 is drawing having shown the result. In drawing 4 - drawing 9, it turns out that the reduction peak to which all appear in 0.6-0.3V is controlled by two or less 100 uA/cm, and the reduction peak of both in connection with an edge face and the Bex Sall side can be controlled by using together with vinylene carbonate.

[0081] (Work examples 7-10)

<Preparation of nonaqueous electrolyte> ethylene carbonate (EC) and methylethyl carbonate (MEC) were mixed at a rate of EC:MEC=4:6 (bulk density), LiPF₆ which are next an electrolyte were dissolved in the nonaqueous solvent, and nonaqueous electrolyte was prepared so that electrolytic concentration might become in l. and 1.0mol /. next, the additive shown in Table 1 to this nonaqueous solvent -- ** -- a fixed quantity was added.

[0082] The <production of negative electrode> natural graphite (product LFmade from China-Vietnam graphite-18A) 87 weight part and the polyvinylidene fluoride (PVDF) 13 weight part of the binder were mixed, N-methyl pyrrolidinone of the solvent was distributed, and natural graphite mixture slurry was prepared. Next, this negative electrode mixture slurry was applied to the 18-micrometer-thick negative electrode current collection object made from band-like copper foil, after making it dry, compression molding was carried out, this was pierced 14mm in the shape of a disc, and the coin-like natural graphite electrode was obtained. The thickness of this natural graphite electrode mixture becomes 110-micron mg/phi, and weight becomes 14mm of 20 mg/phi.

[0083] A <production of LiCoO₂ electrode> LiCoO₂ (product [made from Honjo FMC Energy Systems] HLC-22) 84 weight part, The graphite 9.5 weight part of an electric conduction agent and the acetylene black 0.5 weight part, and the polyvinylidene fluoride 3 weight part of the binder were mixed, N-methyl pyrrolidone of the solvent was distributed, and LiCoO₂ mixture slurry was prepared. 20-micron-thick aluminum foil is made to apply and dry this LiCoO₂ mixture slurry, compression molding is carried out, and omission and LiCoO₂ electrode are produced for this among them to phi13mm. The thickness of this LiCoO₂ mixture becomes 90-micron mg/phi, and weight becomes 13mm of 40 mg/phi.

[0084] A natural graphite electrode with a <production of cell> diameter of 14mm, LiCoO₂ electrode 13mm in diameter, The separator which was able to be done from the fine porosity polypropylene film 25 micrometers in thickness and 16mm in diameter is laminated in order of a natural graphite electrode separator and LiCoO₂ electrode in the battery can of 2032 size made from stainless steel. Then, said 0.03ml of nonaqueous electrolyte is poured into a separator, and it is a plate made from an aluminium (1.2mm in thickness, 16mm in diameter, and a spring were stored.). Finally, through the gasket made from polypropylene, by closing a battery can lid, the airtightness in a cell was held and the coin type cell 20mm in diameter and 3.2mm in height was produced.

[0085] <measurement of the rate of self-discharge at the time of elevated-temperature preservation> -- [the coin cell produced as mentioned above is used, and / this cell] on condition of 0.5mA constant current 4.2V constant voltage It charged until the electric current value at the time of 4.2V constant voltage was set to 0.05mA, and after that, on condition of 1mA constant current 3.0V constant voltage, it discharged until the electric current value at the time of 3.0V constant voltage was set to 0.05mA. Next, on condition of 1mA constant current 3.85V constant voltage, this cell was charged until the electric current value at the time of 3.85V constant voltage was set to 0.05mA. Then, the 45-degree C thermostat performed preservation for this cell for seven days.

[0086] After aging, it discharged to 3.0V and remaining capacity was measured. At this time, self-discharge capacity (= charge capacity-remaining capacity) was calculated as an index showing the self-discharge nature of a cell. The ratio to the amount of self-discharge of an additive-free electrolyte was made into the self-discharge ratio. This self-discharge capacity is an index reflecting the amount of reduction decomposition of the electrolyte in a negative electrode.

[0087] The electrolyte used for the <measurement result of amount of self-discharge> work example and the measurement result of the amount of self-discharge were shown in Table 1.

(Comparative example 3) In the above-mentioned work example 7, omitted addition of the additive, and preparation of nonaqueous electrolyte was performed, and also the cell was produced similarly, and measurement of the amount of self-discharge was measured. The result was shown in Table 1. (Comparative example 4) in the above-mentioned work example 7 -- the time of preparation of nonaqueous electrolyte -- vinylene carbonate -- 1.5wt% -- it added, and also the cell was produced similarly, and measurement of the amount of self-discharge was measured. The result was shown in Table 1.

[Table 1]

| 実施例番号 | 添加剤 | | 自己放電比率 % |
|--------|-----------|-------------------------|-------------|
| | VC wt% | ペーサル面の分解を抑制する化合物 wt% | |
| 実施例 7 | 1.3 | スピロ型ノルボルニル無水こほく酸 0.2 | 6.9 |
| 実施例 8 | 1.0 | スピロ型ノルボルニル無水こほく酸 0.5 | 6.9 |
| 実施例 9 | 1.3 | ビニルエチレンカーボネート 0.2 | 6.9 |
| 実施例 10 | 1.0 | ビニルエチレンカーボネート 0.5 | 7.1 |
| 比較例 3 | 0 | 0 | 10.0 |
| 比較例 4 | 1.5 | 0 | 7.6 |

[0088] The above result showed that the electrolyte of this invention showed the self-discharge inhibition effect which was excellent also in vinylene carbonate independent lay, and the electrolysis of the electrolyte on a negative electrode was controlled further.

[0089]

[Effect of the Invention] By using the nonaqueous electrolyte of this invention, the nonaqueous electrolyte secondary battery with which the reductive cleavage of the electrolyte at the time of elevated-temperature preservation was inhibited can be obtained, and the nonaqueous electrolyte which gives a load characteristic and low-temperature characteristics excellent in the cell is obtained. Moreover, the secondary battery with which the load characteristic and low-temperature characteristics containing this nonaqueous electrolyte have been improved is offered.

[Translation done.]